

# Laser Ablation (LA)-ICP-MS for Production Control of Nickel Alloys

## Application

## Metallurgical Analysis

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### Abstract

**Nickel alloys are used extensively across a wide range of industries, often in components which are required to perform critical functions under arduous operating conditions. As a result, the physical, chemical, and mechanical properties of such alloys must be well understood and the levels of trace metal contaminants, which may have a profound effect on these properties, must be strictly controlled. IncoTest (a business division of Special Metals Wiggin Ltd.) evaluated Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) to monitor and control a wider range of trace elements at lower levels than can be achieved on traditional instrumentation (X-ray Fluorescence and Optical Emission Spectrophotometry). Comparison data obtained using the different techniques is presented, indicating that in all cases, acceptable limits of detection, accuracy, recovery, and long-term stability were obtained using the LA-ICP-MS method.**

### Introduction

Special Metals Corporation purchased the Inco Alloys group of companies in 1998 to become world leader in the invention, production, and supply of high-nickel, high-performance materials including the Nimonic, Inconel, Incoloy, Udimet, Monel, and Nilo alloy groups. It has major manufacturing sites in Huntington, WV and New Hartford, NY in the USA and Hereford in the UK. The IncoTest laboratories offer "state of the art" chemical analysis and mechanical testing in a wide range of different materials.

High temperature Ni alloys belong to a group of materials known as "superalloys". These materials are defined as "alloys developed for elevated temperature service, usually based on Group VIIIA elements, where relatively severe mechanical stressing is encountered and where high surface stability is frequently required" [1]. This describes exactly the conditions that exist inside a gas turbine, and the development of the early Ni alloys was, indeed, driven by the development of the jet engine in the early 1940s. The new alloy materials were developed to withstand the high temperatures, severe mechanical stress, and corrosive environment of various parts of the engine. Different alloys were required for the various components, requiring a detailed understanding of the role of both alloying and impurity elements in determining the physical properties of the alloys.

Superalloys can be broadly divided into three groups: those based on Ni with added Cr, those based on Co, and those based on Fe. There is also a group of Cr-based alloys, but these are not



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typically considered superalloys. While jet engine components remain a key application area for Ni-base superalloys, many other modern uses exist, including marine and land-based gas turbines, components in nuclear reactors and petrochemical plants, rocket engines, space vehicles, and automotive exhausts and catalysts.

Many Ni alloys are strong, but they do not inherently possess the required properties of resistance to high-temperature surface oxidation. The properties of temperature and corrosion resistance are due to the addition of alloying elements, particularly Cr, which forms highly-resistant scales containing  $\text{Cr}_2\text{O}_3$  on the surface of the alloy component. Similarly, strength is increased through the addition of Ti and Al as alloying elements [2]. The precise level of these added elements is critical in providing the required properties for the alloy employed for each specific component. For example, an increase in the level of the hardening elements Al, Ti, and Nb from a total of 16% to a total of 20% results in an alloy that is four times harder. Grain boundaries within the alloy are strengthened through the addition of C and B. The beneficial properties of these and the other most common alloying elements are summarized in Table 1.

In addition to the deliberate addition of alloying elements, which provide beneficial properties not present in the pure Ni material, many other elements may be present at trace levels as contaminants or impurities in the alloy.

Impurity elements, which may be dissolved evenly in the solid alloy matrix or be present as discrete grains or inclusions, can have a dramatic effect on the properties of the final product. For example, Ti, Nb, and Al impurities, in the form of oxide particles, may act as a crack initiator, leading to reduced lifetime and possible failure due to fatigue. Those impurity elements that reduce grain boundary performance and thereby degrade stress-rupture properties include Bi, Te, Se, Pb, and Tl, all of which can have a deleterious effect at concentrations below 100 ppm, with Bi showing the greatest effect at the lowest concentration [3]. Additional elements that reduce malleability and ductility at low concentrations include As, Ba, Ca, Li, Mg, Sb, Sn, and Sr, probably because of their impact on grain-boundary performance.

The typical current specifications for several individual trace impurities in Ni-base superalloys are shown in Table 2, which also shows how these specifications have developed over time, both in terms of the number of elements monitored and also the maximum allowable level of each impurity.

While the detection limits (DLs) of the traditional analytical techniques were adequate to monitor the trace elements at the higher specification levels, with more stringent specifications and reduced allowable levels of impurity elements, new analytical methods were required. Coincidentally, some of the elements that are monitored and controlled at the lowest levels are the most difficult to determine at low levels using optical emission

**Table 1. Purpose of Typical Alloying Elements in Ni-Base Superalloys**

Purpose	Alloying element													
	Cr	Al	Co	Fe	Mo	W	Ti	Ta	Nb	Hf	C	B	Zr	Mg
Matrix strengthener	X		X	X	X	X								
Gamma prime former		X					X	X	X					
Carbide former	X				X	X	X	X	X	X				
Oxide scale former	X	X												
Grain boundary strengthener										X	X	X	X	X

**Table 2. Current and Historic Maximum Impurity Element Levels in Ni-Base Superalloys**

Specification	Impurity element specifications (all values in ppm)												
	Ag	Zn	Cd	Ga	In	Tl	Sn	Pb	As	Sb	Bi	Se	Te
Prior to 1975	5							10			1		
AMS 2280 (1975–1992)													
Total 400 ppm max [4]	50	50	50	50	50	5	50	5	50	50	0.5	3	0.5
Current typical	5	5	0.2	30	0.2	0.2	30	5	30	3	0.5	1	0.5

techniques; these factors led IncoTest to evaluate the potential of LA-ICP-MS for routine monitoring of impurity elements in Ni-alloy production.

The main limitations to the widespread adoption of LA-ICP-MS for the bulk analysis of metals has been the requirement for close matrix matching of the calibration standards to the samples being analyzed, and the fact that most commercial laser systems were designed for the more typical “feature” analysis, for which small crater sizes were beneficial. Nevertheless, facilities to sample over a large area of the sample, using a stored pattern to ablate over a line or area (raster) of the material surface, allowed bulk analysis to be carried out. More recently, a new version of the New Wave UP Series Laser was designed specifically to offer a larger crater size, further increasing the sample area ablated, and it was this new laser that was used in this work. In addition, advances in laser technology, principally towards lower and more consistent energy densities and better ablation stability, now permit a greater variety of materials to be ablated under consistent conditions, allowing calibration across a wider range of materials.

## Experimental

The LA system used for this work was the New Wave UP266 MACRO (New Wave, Fremont, CA, USA) and the ICP-MS system was the Agilent 7500a. The laser method and the ICP-MS tuning and acquisition parameters were set according to manufacturers’ recommendations and the key operating parameters are summarized in Table 3.

**Table 3. Main Operating Parameters for LA-ICP-MS System**

Parameter	Value
<b>New Wave UP266 MACRO</b>	
Spot size (μm)	515
Energy (%)	60
Repetition rate (Hz)	10
Line speed (μm/s)	30
<b>Agilent 7500a</b>	
Forward power (W)	1350
Carrier gas flow (L/min)	1.2

In any ICP-MS analysis of a high matrix sample, some consideration must be given to the potential overlaps and interferences that may occur due to the formation of polyatomic ions. These interferences are derived from the sample matrix and components of the plasma gas plume, which are extracted into the spectrometer. The main potential polyatomic species that might cause such overlaps in the analysis of a Ni alloy material are shown in Table 4.

**Table 4. Principal Matrix-Based Interfering Species in Ni-Matrix Samples**

Matrix interference	Interfered trace element
$^{62}, ^{64}\text{Ni}^{2+}$	$^{31}\text{P}, ^{32}\text{S}$
$^{58}, ^{62}, ^{64}\text{Ni}^1\text{H}^+$	$^{59}\text{Co}, ^{63}, ^{65}\text{Cu}$
$^{60}, ^{61}, ^{62}, ^{64}\text{Ni}^{16}, ^{18}\text{O}^+$	$^{76}, ^{77}, ^{78}, ^{80}, ^{82}\text{Se}$
$^{58}, ^{62}, ^{64}\text{Ni}^{16}\text{O}^1\text{H}^+$	$^{75}\text{As}, ^{79}, ^{81}\text{Br}$
$^{58}, ^{61}\text{Ni}^{40}\text{Ar}^+$	$^{98}\text{Mo}, ^{101}\text{Ru}$
$\text{Ni}_2^+$	$^{118}, ^{120}\text{Sn}, ^{121}, ^{123}\text{Sb}, ^{127}\text{I}, ^{125}, ^{128}\text{Te}$

Most of these interferences form at extremely low levels (for example, oxide interferences are much reduced when sample introduction is by laser, with the consequent elimination of the water vapor associated with solution nebulization), while some others can be easily avoided (such as the analysis of Mo at mass 95, rather than the interfered isotope at mass 98). For the remaining potentially interfered analytes, Ni-alloy producers have well-characterized in-house reference materials with blank levels of the trace elements, so the contribution from the matrix-based polyatomic ion can easily be quantified, corrected, or subtracted.

## Results and Discussion

The method developed for the pre-ablation and acquisition ablation of the Ni-alloy samples was suitable for the sampling of a representative area of the sample surface, although the area sampled was much lower than that measured using Spark, Hollow Cathode, or XRF techniques. While the laser method might therefore have a disadvantage in terms of matching the reproducibility of the “average” signal provided by the larger sampling area of the traditional techniques, it does provide some additional information. The reported mean result at each site is accompanied by a standard deviation (SD), because each 1-cm line scan measurement comprises three separate acquisitions, each of approximately 3-mm length × 0.5-mm width. This triplicate analysis at three different sampling sites provides a mean measured value that is comparable to the Hollow Cathode, but with

additional information on sample homogeneity within each sampled area, which would not be accessible from the simple bulk sampling methods previously used.

The laser sampling method is illustrated in Figure 1, which shows an image of a Ni-alloy sample following ablation using the ablation method described above. Note the grain structure, which is clearly visible in this particular sample.

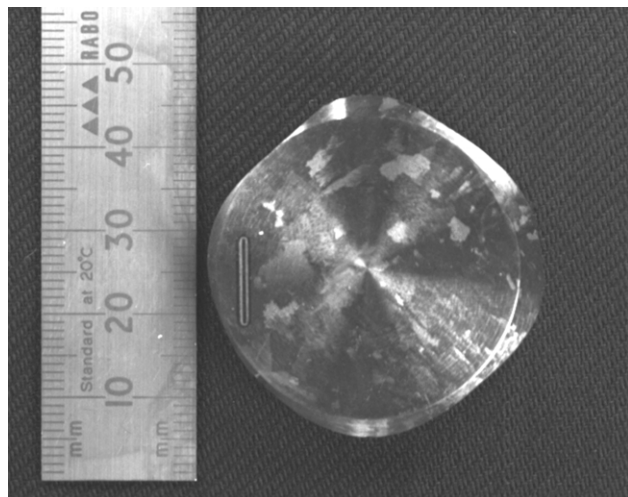


Figure 1. Ni alloy sample following laser ablation analysis.

It was found that severe inhomogeneity in trace element distribution was associated with spiked standards where the trace elements were added at

a much higher concentration than would be present in a normal production sample. Under these circumstances, the trace elements were not fully incorporated in and distributed through the matrix, leading to the presence of nearly pure inclusions of the contaminant elements. These were easily identified from the extremely high standard deviation obtained for LA sample tracks that passed over such inclusions, where one of the replicates was affected by the inclusion and the remaining replicates measured the relatively low “background” analyte signal in the bulk matrix. This information was not available using the traditional analytical techniques, where one or more inclusions would typically be included in every sampling site, giving a more consistent mean result, but no information on trace element distribution or the presence of inclusions.

Where elements were homogeneously distributed through the matrix, precision around 5% RSD was typically achieved from the triplicate analysis at each site. This is illustrated in the calibration plots shown in Figure 2, for the elements Ga and As. In both cases, each calibration standard was analyzed twice and the calibration points are overlaid. Each calibration point is the mean of a triplicate analysis and the error bars indicate the SD of the triplicate analysis (also shown in the data table for the calibration).

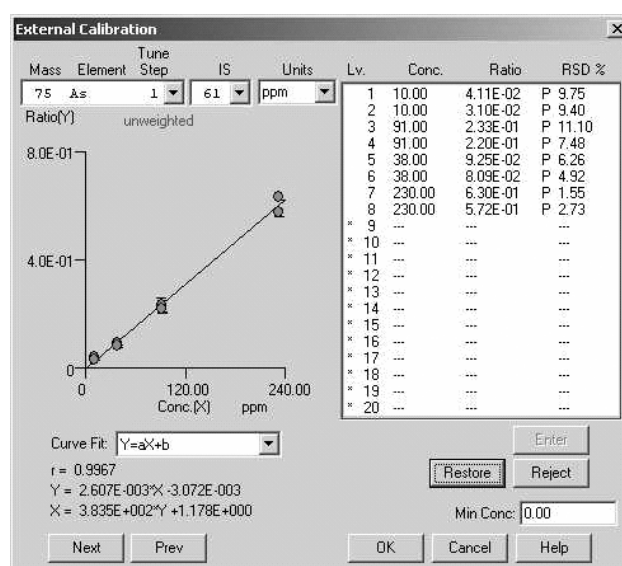
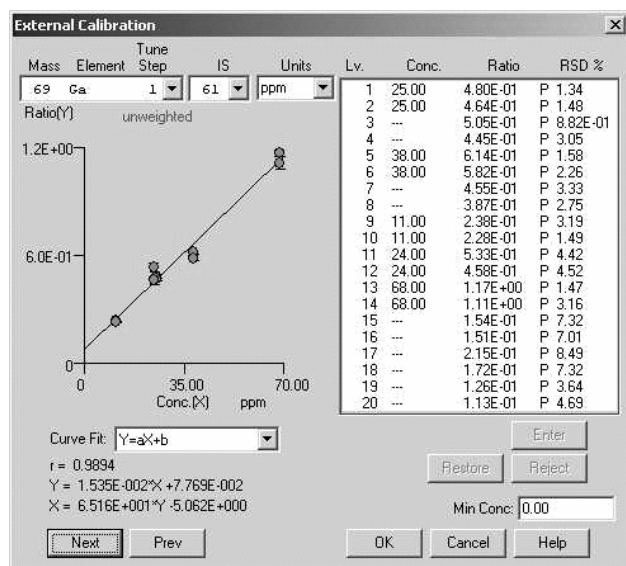


Figure 2. Calibrations for Ga ( $m/z$  69) and As ( $m/z$  75) in Ni-alloy standards by LA-ICP-MS.

In order to validate the new method, LA-ICP-MS data was compared with that from existing analytical methods. The data in Table 5 illustrates the results obtained using the new LA-ICP-MS method for a certified Ni alloy standard material, analyzed over a period of 2 weeks, and compared to the range of results previously obtained by the Hollow Cathode Optical Emission Spectroscopy (OES) method.

From the data in this table, it is apparent that the new LA-ICP-MS method provided consistent results over the analysis period (indeed, with a narrower range of results than the Hollow Cathode method), good internal precision (typically between 5% and 10% RSD), and acceptable agreement with the certified values for this material.

**Table 5. Comparison of Hollow Cathode and LA-ICP-MS Results for Standard 5657 Nimonic-Type Ni-Alloy (Used as a QC Check for Hollow Cathode Analysis)**

Element	Mass	Certified ppm	Hollow Cathode		20-May		25-May LA-ICP-MS		4-Jun	
			Mean ppm	Acceptable Range	Mean ppm	RSD %	Mean ppm	RSD %	Mean ppm	RSD %
<b>Zn</b>	<b>66</b>	<b>22</b>	<b>23</b>	<b>17–30</b>	<b>19.7</b>	<b>4.6</b>	<b>20.6</b>	<b>0.9</b>	<b>18.8</b>	<b>4.2</b>
Ga	69		4.9	2.3–7.5	2	2.7	2.4	4.5	1.3	10.4
<b>As</b>	<b>75</b>	<b>9</b>	<b>10.6</b>	<b>6.7–14</b>	<b>10.8</b>	<b>5</b>	<b>11</b>	<b>5.2</b>	<b>10.6</b>	<b>3.7</b>
Se	82		0.23	0–0.8	1.2	14.5	2.3	8.3	1.3	22.9
<b>Ag</b>	<b>107</b>	<b>9.8</b>	<b>10.6</b>	<b>7.1–14</b>	<b>13</b>	<b>4.6</b>	<b>13</b>	<b>3.6</b>	<b>14.5</b>	<b>3</b>
<b>Cd</b>	<b>111</b>	<b>0.6</b>	<b>0.47</b>	<b>0.3–0.6</b>	<b>0.4</b>	<b>14.2</b>	<b>0.5</b>	<b>6.2</b>	<b>0.8</b>	<b>12.4</b>
In	115		0.01	0–0.03	0.1	13.7	0.1	11	0.1	9.6
<b>Sn</b>	<b>118</b>	<b>53</b>	<b>50</b>	<b>38–62</b>	<b>57</b>	<b>4</b>	<b>56.7</b>	<b>3.9</b>	<b>48.8</b>	<b>4.7</b>
<b>Sb</b>	<b>121</b>	<b>25</b>	<b>21</b>	<b>13–28</b>	<b>28.9</b>	<b>4.5</b>	<b>27.2</b>	<b>2.8</b>	<b>27.7</b>	<b>4.3</b>
Te	125		9	6.4–12	10.7	15.9	8.6	5.6	10.8	9.1
Tl	205		0.18	0–0.25	0.2	3.9	0.2	7.6	0.2	3.8
<b>Pb</b>	<b>208</b>	<b>12</b>	<b>11.5</b>	<b>8.7–14</b>	<b>13.5</b>	<b>4.5</b>	<b>13.8</b>	<b>6.1</b>	<b>15</b>	<b>13.4</b>
<b>Bi</b>	<b>209</b>	<b>8.4</b>	<b>8.8</b>	<b>6.8–11</b>	<b>12</b>	<b>4.75</b>	<b>11.5</b>	<b>5.4</b>	<b>13.2</b>	<b>16.7</b>

## Conclusions

IncoTest have successfully installed and commissioned a LA-ICP-MS system for the routine monitoring of trace element impurities in Ni-base superalloys. In addition to providing acceptable figures of merit for DLs and stability for the trace elements of interest, the new LA-ICP-MS method was also compared to the traditional Hollow Cathode OES method. The new method delivers equivalent results for in-house reference materials, while also providing lower limits of detection for several key contaminant elements and additional information on trace element distribution within the alloy samples.

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